A Study of the Conductivity, Dissociation, and Temperature Coefficients of Conductivity of Certain Inorganic Salts in Aqueous Solution as Conditioned by Temperature, Dilution, Hydration and Hydrolysis

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DISSERTATION

SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES OF THE JOHNS HOPKINS UNIVERSITY IN CONFORMITY WITH THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

BY

EDWARD J. SHAEFFER

BALTIMORE, JUNE, 1913

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Professor Jones, under whose guidance and help this investigation was carried out, deserves special thanks.

A STUDY OF THE CONDUCTIVITY, DISSOCIATION AND TEMPERATURE COEFFICIENTS OF CONDUCTIVITY OF CERTAIN INORGANIC SALTS IN AQUEOUS SOLUTION, AS CONDITIONED BY TEMPERATURE, DILUTION, HYDRATION AND HYDROLYSIS

INTRODUCTION.

The work described in this paper is but a part of the systematic study of the conductivity, dissociation and temperature coefficients of conductivity of electrolytes which was begun in this laboratory twelve years ago in connection with the solvate theory of solution proposed by Jones.[1] In this investigation, inorganic salts have been studied by the modified Kohlrausch conductivity method, and in interpreting the results use has been made of what is known regarding the nature of solution. The theory of electrolytic dissociation,[2] the solvate theory of Jones,[3] the relation pointed out by Dutoit and Aston,[4] connecting the association of a solvent with its dissociating power, and the Thomson[5]-Nernst[6] hypothesis bringing out the relations between dissociating power and dielectric constant of the solvent, offer a satisfactory explanation for a very large part of the conductivity data obtained in this investigation.

HISTORICAL REVIEW

Jones and his coworkers,[7] in discussing conductivity measurements, have given satisfactory reviews of the conductivity work done previous to that carried out in this laboratory. In this review only the work bearing on the conductivity of inorganic compounds in aqueous solutions will be considered. The systematic study of the nature of inorganic salts in aqueous solution, and their dissociation as measured by the modified

[1] Amer. Chem. Journ., **23**, 89 (1900).
[2] Z. physik. Chem., **1**, 631 (1886).
[3] Amer. Chem. Journ., **23**, 103 (1900).
[4] Compt. rend., **125**, 540 (1899).
[5] Phil. Mag., **36**, 320 (1894).
[6] Z. physik. Chem., **13**, 531 (1894).
[7] Amer. Chem. Journ., **34**, 358 (1905); **40**, 355 (1908); **46**, 240 (1911); **48**, 500 (1912)

Kohlrausch conductivity method, was begun by Jones and West in 1904.

It was known that conductivity increased with dilution and rise in temperature, and that the dissociation of electrolytes at high temperatures decreased with rise in temperature, but not much of a reliable nature was known regarding the change in dissociation of electrolytes over the lower temperature ranges with rise in temperature. It was also known that dissociation increased with increase in dilution up to a certain point, where it was complete. For salts, temperature coefficients of conductivity were shown to increase with rise in temperature, while for acids but little change with rise in temperature manifested itself. Satisfactory explanations for most of these facts were lacking. Moreover, the literature contained but a small amount of reliable data regarding the dissociation of important inorganic acids and salts over wide ranges of temperature and dilution. One of the objects in undertaking the investigation was to supply these important data.

Confidence in conductivity methods was greatly strengthened by the work of Jones and West.[1] They did much to improve the accuracy of conductivity measurements. Dissociation over a range of temperature from 0°–35° was found to decrease with rise in temperature. This they pointed out was in accordance with the relation of Dutoit and Aston,[2] connecting the association of a solvent with the dissociation of the dissolved substance. Ramsay and Shields[3] had already pointed out that the association of a solvent decreased with rise in temperature. This result was in accord with the work of von Willer[4] and the Thomson[5]-Nernst[6] hypothesis, which showed that the dissociating power of a solvent increased with its dielectric constant, and that the effect of rise in temperature was to decrease the dielectric constant of the solvent. They found that the percentage temperature coefficients of conductivity

[1] Amer. Chem. Journ., **34,** 357 (1905).
[2] Compt. rend., **125,** 240 (1897).
[3] Z. physik. Chem., **12,** 433 (1893).
[4] Phil. Mag., [6] **7,** 655 (1904).
[5] *Ibid.*, **36,** 320 (1894).
[6] Z. physik. Chem., **13,** 531 (1894).

decreased with rise in temperature, and that the temperature coefficients of conductivity, in the case of salts, increased with rise in temperature, while for acids they decreased.

The work of Jones and his coworkers had already proved that a large number of compounds were hydrated in aqueous solutions, and in Monograph No. 60 of the Publications of the Carnegie Institution of Washington are recorded the approximate compositions of a large number of hydrates. With these conceptions in mind, Jones[1] pointed out a number of relations between conductivity, temperature coefficients of conductivity and the present hydrate theory. Since most ions are hydrated in aqueous solutions, with rise in temperature these unstable hydrates would break down. The effect would be to decrease the mass of the ion, and since the viscosity of the solutions studied changed but slightly with rise in temperature, and the driving power of the current was but little increased, the decreasing mass of the ion is the chief factor in conditioning the increase in conductivity with rise in temperature. It was pointed out that, due to the greater complexity of the hydrates at higher dilutions, we should expect them to change more at high than at low dilutions with rise in temperature. This explains the fact that temperature coefficients of conductivity are greater at high than at low dilutions, and also why the increase in the value of the coefficient is greatest for those substances that have the greatest hydrating power. Jones and Pearce[2] called attention to the fact that the hydrating power of a salt is primarily a function of the cation, and that its ability to hydrate is an inverse function of its atomic volume. Before this relation was pointed out, it was difficult to see how the potassium, rubidium and caesium ions with large atomic volumes could have larger migration velocities than the sodium ions of smaller mass and atomic volume.

Jones and Jacobson[3] continued the work of West. They improved earlier methods and obtained results which substantiated those noted by Jones and West. The effect of

[1] Amer. Chem. Journ., **35**, 445 (1906).
[2] *Ibid.*, **38**, 736 (1907).
[3] *Ibid.*, **40**, 355 (1908).

hydrolysis, acting so as to vitiate the true value of μ_∞, was mentioned. They, furthermore, concluded that salts which are strongly hydrated in solution show a greater increase in conductivity with rise in temperature than salts which are slightly hydrated.

Having these facts in mind, Clover and Jones[1] continued the study of the problem, working at temperatures ranging from 35°–80°. They made it possible to determine conductivities up to a temperature as high as 65°. Certain difficulties, such as the solubility of glass and changes in the cell constants, were overcome. They concluded that it is not practical to measure the conductivity of a solution at 80° unless its concentration is around 0.01 N. The relations pointed out at lower temperatures were also found to hold at higher temperatures. From these results and previous ones, it was now clearly seen that substances with equal hydrating power have approximately the same temperature coefficients of conductivity. As conductivity depends largely on the complexity of the hydrate formed by the ions, we should expect this to be true from the hydrate theory. The sulphates were excepted from the above conclusion, because they are largely polymerized in aqueous solutions. At these temperatures, it was found that dissociation decreased slightly with rise in temperature.

West and Jones[2] continued the work at these high temperatures. They improved still further the methods of measuring conductivity at high temperatures, and obtained results very similar to those found by Clover and Jones.

Hosford and Jones[3] worked at temperatures ranging from 0°–65°. The effect of hydrolysis as causing abnormally great conductivity was pointed out, and it was stated that hydrolysis increases both with dilution and rise in temperature. The effect of hydrolysis on the green variety of chromic salts was shown to be less than on the violet form when the dilution increases. It was suggested that the abnormally rapid increase in conductivity is often caused by a decrease in polymerization. The con-

[1] Amer. Chem. Journ., **43**, 508 (1910).
[2] *Ibid.*, **44**, 508 (1910).
[3] *Ibid.*, **46**, 240 (1911).

ductivity of double salts at temperatures ranging from 0°–65° was found to be less than the sum of the conductivities of the constituent salts, as had been pointed out by Jones and his coworkers[1] at 25°.

Miss Winston and Jones[2] extended the work already done at low temperatures, and their results confirmed those earlier obtained. To account for the increase in percentage dissociation of certain salts with rise in temperature, and large temperature coefficients where there is no reason to expect large hydration, the view that inductive action takes place through the solvent between charged ions and neutral molecules, giving rise to complex ions and molecules in solutions, was advanced by Miss Winston.[2]

The investigation of Howard and Jones[3] continued the work done at higher temperatures. A time factor of hydrolysis was noted, and its effect on conductivity measurements pointed out. This review brings the work up to the present.

Since the beginning of this work, complete conductivity data for 110 of the more common inorganic compounds have been carefully worked out over wide ranges of dilution and temperature. The work has also been extended to about 90 of the more common organic acids. A good idea of the scope of this work may be obtained from a recent publication by Jones[4] and his coworkers in which all the best data obtained thus far have been tabulated and discussed.

PURPOSE OF THIS INVESTIGATION

The object in carrying out this work was to accumulate more data in regard to the dissociation of electrolytes over wide ranges of temperature and dilution, to improve and study the well known Kohlrausch conductivity method as a means of measuring dissociation, to test more fully the conclusions already reached by investigators in this laboratory and to discover new relations from the data obtained.

[1] Amer. Chem. Journ., **19,** 83 (1897); **22,** 5 (1899); **22,** 110 (1899); **25,** 349 (1901).
[2] *Ibid.*, **46,** 368 (1911).
[3] *Ibid.*, **48,** 500 (1912).
[4] Carnegie Institution of Washington, Publication No. **170.**

EXPERIMENTAL DISCUSSION

Apparatus

The Bridge.—About half of the conductivity readings for the lower temperature work were taken from a straight slide wire Wheatstone bridge, calibrated by the method of Strouhal and Barus.[1] The remainder of the work at lower temperatures and all of the work at higher temperatures was done with an improved circular slide wire bridge, made by Leeds and Northrup. By means of this bridge, it was possible to read the resistance of the solution down to fractions of a millimeter.

Rheostat.—The resistance box was standardized against a rheostat which, in turn, had been standardized by the Bureau of Standards in Washington. Considerable stress should be laid upon the necessity of keeping all connections absolutely clean, especially the plugs of the rheostat. The usual methods of cleaning the connections are far from sufficient.

It was found that unless the wires connecting the cells and rheostat were short and of a large diameter, very appreciable errors were introduced in measuring the resistances of concentrated solutions.

Cells.—The cells were of the general types which have been in use in this laboratory for some time. They have recently been described and sketched.[2] As a rule, eight dilutions of each salt were studied, and for each dilution there was a cell the distance between whose electrodes was so arranged that clear minima could be obtained on the bridge. The nine cells had done long service at both high and low temperatures, and from tests it was concluded that practically all soluble matter had been removed from them when heated to temperatures as high as 65°.

During the course of this investigation thirty-five inorganic salts were studied, and the cell constants were taken twenty-three times. No difficulty at all was experienced in keeping the electrode distance of the cells constant for the temperature range 0°–35°. Clover and Jones[3] and West and Jones[4]

[1] Wied. Ann., **10,** 32 (1880).
[2] Carnegie Institution of Washington, Publication No. **170,** p. 5.
[3] Amer. Chem. Journ., **43,** 195 (1910).
[4] *Ibid.*, **44,** 511 (1910).

experienced difficulty in keeping the electrode distance of the cells constant for the temperature range 35°–65°. Their recommendations were carefully adhered to. At the very beginning of the work at high temperatures, the cell constants were found to undergo change. It was caused, no doubt, by forcing the ground glass stoppers too tightly into the cell cups. At 50° and 65°, the accumulated pressure would at times force the stoppers out of the cells, and invariably the electrode distance was disturbed. This was easily overcome by loosely stoppering the cells, and the work done at this period was repeated.

The cell constants were always determined at 25°. To determine the constants of the four cells with the greatest electrode distance, a 0.02 N potassium chloride solution was used. Its conductivity was taken as 129.7. To determine the constants of the remaining four cells, a 0.002 N solution of potassium chloride was used. Its conductivity value was determined several times and always found to be close to 135.5 For the water cell a 0.001 N potassium chloride solution was used. Its conductivity was usually close to 140.

Baths.—The baths used to maintain constant temperature were of the type described by Jones.[1] For the higher temperature work, an efficient cover was devised[2] which served to keep the temperature of the air above the cells at about the same temperature as the water surrounding the cells. During conductivity measurements the water contained in the bath was actively stirred by means of a hot air engine. The thermometers were carefully calibrated against standard ones. During part of the work, the temperature of the baths was regulated by means of thermoregulators similar to the type devised by Reid.[3] For the most part, however, the temperatures were regulated by hand.

Containing Vessels.—All flasks and burettes were calibrated and recalibrated by the method of Morse and Blalock.[4] In addition, the 1000 cc. and 500 cc. flasks used to measure

[1] Carnegie Institution of Washington, Publication No. **170**, p. 9.
[2] Amer. Chem. Journ., **48**, 504 (1912).
[3] *Ibid.*, **41**, 148 (1909).
[4] *Ibid.*, **16**, 479 (1894).

the volume of the mother solution were calibrated also by the weight method, and very close agreements with the method of Morse and Blalock were obtained. For the higher temperature work, all containing vessels were of Jena glass. How slightly soluble this glass is will be brought out in a later connection. The 500 cc. flask used for this work was calibrated so that when it was filled to the proper mark at 20° it would contain 500 cc. of solution at 50°.[1]

Preparation of Solutions.—Whenever a salt was used at both high and low temperatures, two sets of solutions were prepared. The conductivities of both sets were determined at 35°, and thus a check upon our work was obtained. The solutions used for the lower temperature work were made up at 20°.

Since the volume changes of a solution are so great with change in temperature, one is obviously at a great disadvantage in making up solutions at temperatures very far removed from that of the room. At high temperatures, it is a well known fact that the solubility of the glass is another factor which must be taken into account. Methods described by West and Jones[2] and by Springer and Jones[3] made it possible to prepare solutions at 20° and to use these solutions for conductivity determinations at 35°, 50° and 65°.

For the high temperature work, the solutions were made up from a mother solution contained in a specially calibrated 500 cc. flask. This flask had two marks. To determine the position of the lower mark the weight of 500 cc. of distilled water at 50°, air displacement being taken into account, was used. When this flask was filled with a solution up to the mark at 20° and then warmed to 50° it contained just 500 cc. at 50°. To test the correctness of the above mark, the flask was calibrated by the method of Morse and Blalock so as to contain 500 cc. at 50°. Of course, the proper corrections for these calibrations were taken into account. When a solution at 20° was added to the flask up to the 20° mark and heated to 50°, it was found

[1] Amer. Chem. Journ., **48**, 417 (1912).
[2] *Ibid.*, **44**, 508 (1910).
[3] *Ibid.*, **48**, 416 (1912).

that its meniscus corresponded with the calibration mark at 50° determined by the method of Morse and Blalock. With but very few exceptions, the coefficients of expansion of our most concentrated solutions were only slightly different from that of distilled water. It was thus made certain that the solutions, made up at 20°, would be of the proper concentration when heated to 50°. To correct for the increase in concentration due to cooling such a solution down from 50° to 35°, the factor 0.994, as worked out by Jones and Clover,[1] was multiplied into all conductivity values obtained at 35°. The factor 1.0076,[2] when multiplied into the conductivities obtained at 65°, corrected for the decrease in concentration due to warming the solutions from 50° to 65°.

Purification of Salts.—Nearly every salt worked with in this investigation came from Kahlbaum. Just how each salt was purified and the concentration of the mother solution determined is stated above the conductivity tables for that particular salt. It is desirable to do this in some detail, since conductivity data obtained by different investigators for the same substance are often discordant, and unless the investigator makes known the method of purification, and the way in which the concentration of the mother solution was ascertained, it is difficult to tell which values are more likely to be correct. Such information is certainly of great assistance to other investigators in this field.

Conductivity Water.—All the water used in this work was purified by the method of Jones and Mackay.[3] The water thus obtained had an average conductivity of 0.7×10^{-6} at 0°.

The conductivity data are expressed in Siemens units according to well known methods of calculation.[4] Each conductivity value recorded is the average of three readings.

Ammonium Hydrogen Sulphate

The above salt was recrystallized from conductivity water. The exact strength of the mother solution was determined

[1] Amer. Chem. Journ., **43**, 187 (1910).
[2] *Ibid.*, **44**, 510 (1910).
[3] *Ibid.*, **19**, 91 (1897).
[4] Carnegie Institution of Washington, Publication No. **170**, p. 11.

by precipitation of the sulphuric acid by means of barium chloride.

Table I.—Conductivity and Dissociation

	35°		50°		65°	
V	μ_v	α	μ_v	α	μ_v	α
2	207.2	35.9	223.8	31.4	235.3	27.5
8	263.5	45.6	286.0	40.1	303.2	35.5
32	339.2	58.8	374.2	52.5	396.5	46.4
128	433.9	75.2	485.9	68.2	525.3	61.4
512	510.2	88.4	593.5	83.3	666.1	77.9
1024	543.9	94.2	647.1	90.8	794.5	93.0
2048	560.0	97.0	681.5	95.6	820.6	96.0
4096	577.2	100.0	712.5	100.0	855.2	100.0

Table II.—Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
2	1.11	0.54	0.77	0.34
8	1.50	0.57	1.15	0.40
32	2.33	0.69	1.49	0.40
128	3.47	0.80	2.63	0.54
512	5.55	1.08	4.84	0.82
1024	6.88	1.26	9.83	1.52
2048	8.10	1.25	9.27	1.36
4096	9.02	1.56	8.85	1.23

Tetraethylammonium Iodide

The mother solution was standardized by weighing the dry and purified salt.

Table III.—Conductivity

V	0°	12°.5	25°	35°
8	38.6	54.6	72.8	88.5
32	46.5	65.4	86.8	105.0
128	51.1	72.1	95.4	114.8
512	52.8	73.9	98.0	118.4
1024	53.3	75.2	99.3	119.7
2048	54.4	77.0	101.7	122.5
4096	54.0	76.5	101.6	122.9

Table IV.—Temperature Coefficients

	0°–12°.5		12°.5–25°		25°–35°	
V	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
8	1.28	3.31	1.46	2.67	1.57	2.15
32	1.51	3.25	1.70	2.60	1.82	2.09
128	1.67	3.29	1.86	2.56	1.94	2.03
512	1.69	3.20	1.92	2.59	2.04	2.08
1024	1.76	3.20	1.93	2.58	2.04	2.07
2048	1.78	3.27	1.98	2.57	2.08	2.04
4096	1.80	3.32	2.00	2.61	2.12	2.08

Table V.—Percentage Dissociation

V	0°	12°.5	25°	35°
8	70.9	70.9	71.6	72.0
32	85.5	84.9	85.3	85.4
128	93.1	93.6	93.7	93.4
512	97.1	95.9	96.3	96.3
1024	98.0	97.7	97.6	97.5
2048	100.0	100.0	100.0	99.7
4096	99.2	99.4	99.9	100.0

Ammonium Sodium Hydrogen Phosphate

It was found that concentrated solutions of this salt decomposed at about 25°. For that reason it could not be safely purified by ordinary methods. The phosphoric acid in the mother solution was determined by means of magnesia mixture.

Table VI.—Conductivity

V	0°	12°.5	25°	35°
8	65.6	...	...	...
32	84.4	119.2	158.7	186.5
128	96.5	136.7	181.4	216.6
512	100.7	141.4	186.4	221.6
1024	104.7	145.7	193.6	235.2
2048	103.9	144.7	190.9	229.2

Table VII.—Temperature Coefficients

	0°–12°.5		12°.5–25°		25°–35°	
V	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
32	2.78	3.30	3.16	2.65	2.78	1.49
128	3.21	3.32	3.57	2.61	3.52	1.62
512	3.26	3.24	3.60	2.54	3.52	1.58
1024	3.36	3.22	3.83	2.62	4.16	1.76
2048	3.36	3.22	3.70	2.55	3.83	1.67

Table VIII.—Percentage Dissociation

V	0°	12°.5	25°	35°
8	62.6	...	...	...
32	80.6	81.7	81.9	79.3
128	91.3	93.1	93.7	92.1
512	96.3	97.0	96.2	94.2
1024	100.0	100.0	100.0	100.0
2048	99.2	99.3	98.6	97.4

Sodium Chloride

This salt was twice recrystallized from concentrated solutions by the addition of purified hydrochloric acid gas. It was then dried in an air bath for six hours at about 260°.

Table IX.—Conductivity

V	0°	12°.5	25°	35°
2	48.1	66.4	86.5	104.2
8	53.5	74.7	98.5	118.5
32	57.5	80.6	106.8	129.5
128	60.4	84.9	112.6	136.3
512	62.3	87.8	116.4	141.2
1024	61.6	86.9	115.4	140.0

Table X.—Temperature Coefficients

	0–12°.5		12°.5–25°		25°–35°	
V	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
2	1.46	3.04	1.61	2.44	1.77	2.05
8	1.70	3.19	1.90	2.54	2.00	2.03
32	1.85	3.21	2.09	2.59	2.27	2.12
128	1.96	3.24	2.21	2.60	2.37	2.11
512	2.04	3.27	2.29	2.61	2.48	2.13
1024	2.02	3.28	2.28	2.62	2.46	2.13

Table XI.—Percentage Dissociation

V	0°	12°.5	25°	35°
2	77.2	75.6	74.4	73.8
8	85.9	85.1	84.6	83.9
32	92.3	91.8	91.7	91.6
128	96.9	96.7	96.6	96.5
512	100.0	100.0	100.0	100.0
1024	98.9	99.0	99.1	99.1

Sodium Chlorate

The purified salt was dried in an air bath for two hours at 110°.

Table XII.—Conductivity

V	0°	12°.5	25°	35°
2	41.6	57.5	74.7	90.0
8	47.4	66.1	86.7	104.4
32	51.7	72.4	95.0	115.2
128	54.7	76.9	101.1	122.5
512	56.0	78.9	104.6	127.0
1024	56.2	79.0	104.1	126.3
2048	56.1	78.8	104.1	125.8

Table XIII.—Temperature Coefficients

	0°–12°.5		12°.5–25°		25°–35°	
V	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
2	1.27	3.05	1.38	2.40	1.53	2.04
8	1.50	3.12	1.66	2.41	1.77	2.05
32	1.66	3.21	1.80	2.49	2.02	2.12
128	1.78	3.25	1.94	2.53	2.14	2.12
512	1.83	3.26	2.05	2.64	2.36	2.25
1024	1.82	3.24	2.01	2.54	2.22	2.13
2048	1.81	3.22	2.02	2.56	2.17	2.09

Table XIV.—Percentage Dissociation

V	0°	12°.5	25°	35°
2	74.0	72.8	71.4	70.8
8	84.3	83.6	82.9	81.4
32	91.9	91.6	90.8	90.7
128	97.3	97.3	96.6	96.4
512	99.6	99.8	100.0	100.0
1024	100.0	100.0	99.5	99.5
2048	99.7	99.7	99.5	99.0

Sodium Chlorate

The purified salt was dried in an air bath for two hours at 110.°

Table XV.—Conductivity and Dissociation

	35°		50°		65°	
V	μ_v	α	μ_v	α	μ_v	α
8	103.7	79.5	132.1	78.5	164.4	77.7
32	118.0	90.4	151.6	90.0	186.3	88.1
128	122.9	94.2	158.4	94.1	198.7	94.0
312	126.1	96.6	165.2	98.1	204.4	96.7
1024	130.2	99.8	167.8	99.6	211.3	100.0
2048	130.5	100.0	168.3	100.0	209.1	99.0

Table XVI.—Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
8	1.90	1.89	2.15	1.62
32	2.24	1.94	2.31	1.52
128	2.39	1.94	2.68	1.69
512	2.54	2.00	2.61	1.58
1024	2.51	1.93	2.90	1.78
2048	2.52	1.93	2.72	1.62

Sodium Perchlorate

After being recrystallized, the purified product was dried to constant weight in a weighing tube at 140°. The weighing tube was used because the salt was found to be somewhat deliquescent.

Table XVII.—Conductivity

V	0°	12°.5	25°	35°
8	49.5	69.0	90.3	109.1
32	53.5	74.9	98.5	119.2
128	56.3	78.9	104.2	126.1
512	57.0	80.0	105.7	128.8
1024	59.6	83.6	109.2	132.6
2048	60.01	84.4	111.5	135.4
4096	60.05	85.9	114.3	139.1

Table XVIII.—Temperature Coefficients

	0°–12°.5		12°.5–25°		25°–35°	
V	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
8	1.56	3.15	1.70	2.46	1.88	2.08
32	1.71	3.18	1.88	2.51	2.07	2.10
128	1.81	3.21	2.02	2.56	2.19	2.10
512	1.83	3.21	2.05	2.56	2.31	2.18
1024	1.92	3.24	2.05	2.45	2.34	2.14
2048	1.95	3.25	2.17	2.57	2.39	2.14
4096	2.07	3.44	2.27	2.65	2.48	2.17

Table XIX.—Percentage Dissociation

V	0°	12°.5	25°	35°
8	82.4	80.3	79.0	78.4
32	89.1	87.2	86.2	85.7
128	93.7	91.8	91.1	90.7
512	98.6	95.2	94.4	92.6
1024	99.2	97.3	95.5	95.3
2048	99.9	98.2	97.5	97.4
4096	100.0	100.0	100.0	100.0

Sodium Perchlorate

The mother solution for this series was prepared in exactly the same way as that for the series at lower temperatures. The specimen of salt used was not the same as that used for the lower temperature work.

Table XX.—Conductivity and Dissociation

	35°		50°		65°	
V	μ_v	α	μ_v	α	μ_v	α
8	109.3	80.9	139.6	80.2	171.5	79.9
32	119.1	88.2	152.4	87.6	187.6	87.4
128	125.5	93.0	160.7	92.4	198.4	92.4
512	129.5	95.9	166.7	95.8	205.9	95.9
1024	132.0	97.8	170.4	97.9	211.3	98.4
2048	133.8	99.1	170.6	98.0	212.5	99.0
4096	135.0	100.0	173.9	100.0	214.6	100.0

Table XXI.—Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
8	2.02	1.85	2.13	1.53
32	2.22	1.86	2.35	1.54
128	2.35	1.87	2.51	1.59
512	2.48	1.91	2.61	1.57
1024	2.56	1.94	2.73	1.60
2048	2.45	1.83	2.79	1.63
4096	2.59	1.92	2.71	1.56

Disodium Hydrogen Phosphate

The specimen of salt used was three times recrystallized. By precipitation of the phosphorus as magnesium pyrophosphate, the exact strength of the mother solution was ascertained.

Table XXII.—Conductivity and Dissociation

	35°		50°		65°	
V	μ_v	α	μ_v	α	μ_v	α
16	164.3	68.4	215.3	68.2	268.5	67.3
32	182.4	75.9	238.7	75.6	298.9	74.9
128	212.1	88.3	278.4	88.2	350.9	87.9
512	231.6	96.4	304.7	96.5	384.6	96.4
1024	236.4	98.4	310.2	98.3	393.2	98.5
2048	240.3	100.0	315.6	100.0	399.0	100.0

Table XXIII.—Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
16	3.40	2.07	3.55	1.65
32	3.75	2.06	4.02	1.69
28	4.42	2.08	4.83	1.73
512	4.87	2.10	5.33	1.75
1024	4.92	2.08	5.53	1.78
2048	5.02	2.09	5.56	1.76

Potassium Chlorate

The specimen used was recrystallized and dried in an air bath for two hours at 120°. The strength of the mother solution was obtained by weighing the pure and dry salt.

Table XXIV.—Conductivity

V	0°	12°.5	25°	35°
8	58.9	80.8	104.7	124.9
32	64.3	88.3	115.2	137.3
128	68.5	94.2	122.8	146.5
512	70.1	96.7	126.1	150.9
1024	70.6	97.7	127.8	153.1
2048	71.2	98.4	128.4	154.0
4096	72.4	100.7	131.4	157.6

Table XXV.—Temperature Coefficients

	0°–12°.5		12°.5–25°		25°–35°	
V	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
8	1.75	2.97	1.91	2.36	2.02	1.93
32	1.94	3.00	2.15	2.43	2.21	1.93
128	2.07	2.90	2.29	2.42	2.36	1.92
512	2.12	3.02	2.35	2.43	2.48	1.95
1024	2.15	3.04	2.42	2.47	2.52	1.97
2048	2.18	3.06	2.44	2.47	2.56	1.98
4096	2.25	3.09	2.46	2.44	2.62	1.98

Table XXVI.—Percentage Dissociation

V	0°	12°.5	25°	35°
8	81.3	80.2	79.7	79.2
32	88.8	87.6	87.5	87.1
128	94.6	93.5	93.2	92.9
512	96.8	96.0	95.9	95.7
1024	97.5	97.2	97.2	97.1
2048	98.3	97.7	97.7	97.7
4096	100.0	100.0	100.0	100.0

Potassium Chlorate

The specimen of salt used for this series was the same as that used for the work at lower temperatures. It was purified and standardized in exactly the same way as above.

Table XXVII.—Conductivity and Dissociation

	35°		50°		65°	
V	μ_v	α	μ_v	α	μ_v	α
8	125.4	78.3	158.6	77.6	192.1	76.8
32	137.3	85.8	173.4	84.9	211.9	84.8
128	146.4	91.4	185.0	90.6	228.8	91.6
512	151.2	94.4	193.4	94.6	239.1	95.7
1024	153.1	95.6	197.4	96.6	241.5	96.7
2048	158.1	98.7	200.8	98.2	244.9	98.0
4096	160.1	100.0	204.3	100.0	249.7	100.0

Table XXVIII.—Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
8	2.22	1.77	2.23	1.40
32	2.41	1.76	2.57	1.48
128	2.57	1.76	2.92	1.57
512	2.81	1.85	3.05	1.57
1024	2.95	1.92	2.94	1.49
2048	2.85	1.80	2.94	1.46
4096	2.95	1.84	3.03	1.48

Potassium Perchlorate

This salt received two crystallizations. It was dried in the air bath for two hours at 130°.

Table XXIX.—Conductivity

V	0°	12°.5	25°	35°
32	65.1	89.8	116.9	139.6
128	68.9	95.0	125.1	149.5
512	71.7	98.2	129.0	154.2
1024	72.0	99.5	130.7	155.3
2048	73.3	101.2	132.6	158.6
4096	74.3	102.6	134.5	160.7

Table XXX.—Temperature Coefficients

	0°–12°.5		12°.5–25°		25°–35°	
V	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
32	1.98	3.04	2.17	2.42	2.27	1.94
128	2.08	3.02	2.40	2.52	2.44	1.95
512	2.12	2.95	2.44	2.60	2.52	1.95
1024	2.20	3.05	2.49	2.50	2.56	1.95
2048	2.23	3.04	2.51	2.48	2.60	1.96
4096	2.26	3.04	2.55	2.49	2.62	1.94

Table XXXI.—Percentage Dissociation

V	0°	12°.5	25°	35°
32	87.6	87.6	86.9	86.9
128	92.7	92.5	93.0	93.0
512	96.5	95.7	95.9	95.3
1024	97.0	96.9	97.1	96.6
2048	98.6	98.5	98.5	98.6
4096	100.0	100.0	100.0	100.0

Potassium Perchlorate

The values given below were obtained from the same sample of salt as was used at lower temperatures. As before, it was recrystallized and dried in the air bath for two hours at 130°.

Table XXXII.—Conductivity and Dissociation

	35°		50°		65°	
V	μ_v	α	μ_v	α	μ_v	α
32	139.8	85.8	178.0	86.2	217.2	86.4
128	150.3	92.3	190.2	92.1	232.7	92.6
512	153.9	94.5	194.3	94.1	237.7	94.6
1024	155.0	95.1	195.9	94.9	240.6	95.7
2048	157.5	96.7	200.0	96.9	244.2	97.2
4096	162.9	100.0	206.4	100.0	251.3	100.0

The conductivity values given by Ostwald for this salt are several units higher than those here recorded. Several of the above values were redetermined with a new specimen of pure potassium perchlorate, and very close agreements with the above values were obtained.

Table XXXIII.—Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
32	2.55	1.81	2.61	1.46
128	2.66	1.77	2.83	1.48
512	2.69	1.75	2.89	1.48
1024	2.73	1.76	2.98	1.52
2048	2.83	1.79	2.94	1.42
4096	2.90	1.78	2.99	1.44

Potassium Phosphate

The phosphorus content of the original solution was determined by means of magnesia mixture. Different specimens from Kahlbaum were used for the low and high temperature work.

Table XXXIV.—Conductivity

V	0°	12°.5	25°	35°
8	116.6	163.8	217.2	263.6
32	144.1	206.7	280.3	344.2
128	178.9	257.7	348.2	425.2
512	193.7	274.7	366.1	442.8
1024	192.1	271.5	362.5	440.1
2048	190.0	268.3	359.3	437.2
4096	179.0	252.0	336.7	407.6

Table XXXV.—Temperature Coefficients

	0°–12°.5		12°.5–25°		25°–35°	
V	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
8	3.78	3.24	4.27	2.60	4.64	2.13
32	5.00	3.54	5.88	2.85	6.39	2.24
128	6.30	3.50	7.24	2.81	7.70	2.21
512	6.48	3.34	7.31	2.66	7.67	2.10
1024	6.35	3.30	7.28	2.68	7.76	2.14
2048	6.26	3.29	7.28	2.75	7.79	2.14
4096	5.84	3.27	6.78	2.69	7.09	2.10

Table XXXVI.—Percentage Dissociation

V	0°	12°.5	25°	35°
8	60.2	59.6	59.3	59.5
32	74.4	75.2	76.5	77.7
128	92.9	93.8	95.1	96.0
512	100.0	100.0	100.0	100.0
1024	99.2	98.8	99.0	99.3
2048	98.0	97.3	98.1	98.7
4096	92.4	92.1	91.9	92.0

Potassium Phosphate

Table XXXVII.—Conductivity and Dissociation

	35°		50°		65°	
V	μ_v	α	μ_v	α	μ_v	α
8	261.4	58.9	334.5	58.2	415.5	58.7
32	346.9	78.4	453.6	78.7	566.1	80.0
128	427.8	96.4	552.2	96.1	685.7	96.9
512	443.7	100.0	574.6	100.0	707.6	100.0
1024	439.8	99.1	565.1	98.3	697.3	98.5
2048	426.0	96.0	549.5	95.6	676.2	95.5
4096	402.5	90.9	517.1	90.0	646.9	91.4

Table XXXVIII.—Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
8	4.87	1.86	5.40	1.61
32	7.11	2.05	7.50	1.65
128	8.29	1.94	8.90	1.61
512	8.73	1.96	8.87	1.54
1024	8.35	1.89	8.81	1.56
2048	8.23	1.93	8.45	1.53
4096	7.64	1.89	8.65	1.67

Calcium Chloride

The specimen of salt used was purified by two recrystallizations from conductivity water. The concentration of the mother solution was ascertained by weighing calcium as the oxide, CaO.

Table XXXIX.—Conductivity

V	0°	12°.5	25°	35°
2	80.5	109.6	142.1	169.1
8	95.3	132.1	172.5	207.4
32	106.4	149.3	197.5	238.0
128	117.8	165.6	219.2	265.8
512	124.0	174.8	232.4	281.9
1024	126.5	179.0	236.1	284.6
2048	131.4	185.0	245.0	298.3
4096	131.3	185.2	246.5	300.0

Table XL.—Temperature Coefficients

	0°–12°.5		12°.5–25°		25°–35°	
V	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
2	2.32	2.90	2.60	2.46	2.70	1.90
8	2.94	3.08	3.23	2.44	3.49	2.02
32	3.43	3.21	3.85	2.58	4.05	2.05
128	3.82	3.24	4.29	2.58	4.66	2.12
512	4.06	3.27	4.57	2.61	4.94	2.12
1024	4.20	3.39	4.70	2.68	4.85	2.05
2048	4.28	3.02	4.80	2.58	5.33	2.17
4096	4.31	3.26	4.90	2.59	5.35	2.17

Table XLI.—Percentage Dissociation

V	0°	12°.5	25°	35°
2	61.2	59.1	57.6	56.3
8	72.5	71.3	69.9	69.1
32	80.9	80.6	80.1	79.3
128	89.6	89.4	88.9	88.6
512	94.3	94.2	94.6	93.9
1024	96.2	96.1	95.7	94.8
2048	100.0	100.0	99.3	99.4
4096	99.9	99.9	100.0	100.0

Strontium Chloride

After the salt had been subjected to three recrystallizations the chlorine content in the mother solution was determined as silver chloride.

Table XLII.—Conductivity and Dissociation

	35°		50°		65°	
V	μ_v	α	μ_v	α	μ_v	α
8	208.9	68.8	265.5	67.7	324.4	66.6
16	224.5	73.9	285.6	72.8	350.2	71.9
32	240.4	79.1	305.7	77.9	377.5	77.5
128	267.3	88.0	342.4	87.3	424.6	87.2
512	282.8	93.1	367.7	93.7	453.9	93.2
1024	286.8	94.4	373.0	95.1	463.3	95.2
2048	297.0	97.8	383.2	97.7	476.5	97.8
4096	303.7	100.0	392.2	100.0	486.9	100.0

Table XLIII.—Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
8	3.78	1.81	3.92	1.48
16	4.07	1.81	4.25	1.49
32	4.35	1.81	4.79	1.56
128	5.01	1.87	5.48	1.60
512	5.66	2.00	5.75	1.57
1024	5.75	2.01	6.02	1.62
2048	5.75	1.94	6.22	1.62
4096	5.90	1.94	6.32	1.61

Barium Bromide

After careful recrystallization of the salt, the exact barium content in the mother solution was determined as barium sulphate.

Table XLIV.—Conductivity and Dissociation

	35°		50°		65°	
V	μv	α	μv	α	μv	α
8	222.0	70.5	280.1	69.2	340.1	68.4
16	237.8	75.6	301.1	74.4	367.6	73.9
32	251.8	80.0	320.2	79.1	392.8	79.0
128	278.4	88.5	358.0	88.5	439.2	88.3
512	295.1	93.8	379.6	93.8	467.6	94.0
1024	302.1	96.0	385.3	95.2	475.1	95.5
2048	305.5	97.1	393.9	97.4	484.6	97.4
4096	314.7	100.0	404.5	100.0	497.2	100.0

Table XLV.—Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
8	3.87	1.74	4.00	1.42
16	4.22	1.77	4.43	1.47
32	4.56	1.81	4.84	1.51
128	5.31	1.91	5.41	1.51
512	5.63	1.91	5.87	1.54
1024	5.55	1.83	5.99	1.55
2048	5.90	1.93	6.05	1.54
4096	5.65	1.80	6.18	1.53

Barium Formate

The above salt was three times recrystallized. The concentration of the barium in the original solution was determined by weighing the barium as barium sulphate.

Table XLVI.—Conductivity and Dissociation

	35°		50°		65°	
V	μv	α	μv	α	μv	α
8	158.8	66.1	201.0	64.2	245.4	63.6
16	178.4	74.3	227.3	72.6	275.1	71.4
32	196.6	81.9	252.1	80.5	307.3	79.7
128	225.4	93.8	289.6	92.4	359.6	93.3
512	237.8	99.0	308.2	98.4	383.6	99.5
1024	240.1	100.0	313.2	100.0	385.5	100.0
2048	239.8	99.9	309.5	98.8	376.4	97.6

Table XLVII.—Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
8	2.81	1.77	2.96	1.47
16	3.26	1.83	3.19	1.43
32	3.70	1.88	3.68	1.46
128	4.28	1.89	4.67	1.61
512	4.69	1.97	5.03	1.63
1024	4.87	2.03	4.82	1.54
2048	4.65	1.94	4.46	1.44

Magnesium Chloride

The above salt was purified by three crystallizations. Precipitations of the magnesium as magnesium pyrophosphate determined the strength of the mother solution.

Table XLVIII.—Conductivity

V	0°	12°.5	25°	35°
4	80.2	112.1	147.3	177.6
8	87.6	123.2	162.1	196.1
32	100.0	141.1	187.1	226.4
128	110.2	156.1	208.0	252.4
512	115.7	164.3	219.4	266.8
1024	118.3	168.5	225.0	272.2
2048	120.2	172.8	230.2	280.0
4096	123.5	176.3	234.7	285.2

Table XLIX.—Temperature Coefficients

	0°–12°.5		12°.5–25°		25°–35°	
V	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
4	2.55	3.17	2.82	2.51	3.03	2.05
8	2.85	3.25	3.11	2.52	3.40	2.09
32	3.29	3.29	3.68	2.60	3.93	2.10
128	3.67	3.33	4.15	2.65	4.44	2.13
512	3.89	3.36	4.41	2.67	4.74	2.16
1024	4.02	3.39	4.52	2.68	4.72	2.09
2048	4.21	3.48	4.59	2.65	4.98	2.16
4096	4.22	3.32	4.67	2.64	5.05	2.15

Table L.—Percentage Dissociation

V	0°	12°.5	25°	35°
4	64.9	63.6	62.8	62.3
8	70.9	69.9	69.1	68.7
32	80.9	80.0	79.7	79.4
128	89.2	88.5	88.6	88.5
512	93.7	93.2	93.5	93.5
1024	95.8	95.6	95.8	95.4
2048	97.3	98.0	98.1	98.2
4096	100.0	100.0	100.0	100.0

Magnesium Sulphate

This salt was recrystallized three times. An attempt was made to get the purified and dried product anhydrous by heating it in an air bath for two hours at 225°. It was found that the anhydrous salt readily took up moisture from the air, and, furthermore, that the salt could not be obtained perfectly anhydrous at temperatures even higher than that stated above. Consequently, the mother solution was standardized by analysis, the sulphur being precipitated as barium sulphate.

Table LI.—Conductivity and Dissociation

	35°		50°		65°	
V	μ_v	α	μ_v	α	μ_v	α
2	72.4	27.6	90.5	26.5	106.5	25.2
8	104.0	39.6	131.0	38.3	155.4	36.8
16	120.4	45.8	150.7	44.1	179.0	42.4
32	139.0	52.9	174.6	51.1	208.6	49.4
128	180.7	68.8	230.3	67.4	279.1	66.0
512	224.7	85.6	288.1	84.3	353.1	83.6
1024	245.9	93.6	317.7	93.0	395.4	93.6
2048	262.6	100.0	341.7	100.0	422.6	100.0

Table LII.—Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
2	1.21	1.67	1.07	1.18
8	1.80	1.73	1.63	1.24
16	2.02	1.68	1.89	1.27
32	2.37	1.71	2.27	1.30
128	3.31	1.83	3.25	1.41
512	4.23	1.88	4.32	1.50
1024	4.79	1.95	5.18	1.63
2048	5.27	2.01	5.39	1.58

Manganous Chloride

After the salt had been twice recrystallized from conductivity water, the manganese in the original solution was determined as the pyrophosphate.

Table LIII.—Conductivity and Dissociation

	35°		50°		65°	
V	μ_v	α	μ_v	α	μ_v	α
2	142.5	49.3	177.3	47.5	210.5	44.9
8	191.5	66.3	242.3	64.9	293.7	62.7
16	210.3	72.8	266.8	71.5	326.6	69.7
32	226.5	78.4	289.1	77.5	357.0	76.2
128	252.9	87.6	325.0	87.2	402.3	85.9
512	274.7	95.1	356.2	95.5	447.4	95.5
1024	281.3	97.4	366.4	98.3	459.2	98.1
2048	288.8	100.0	372.9	100.0	468.4	100.0

Table LIV.—Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
2	2.32	1.63	2.21	1.25
8	3.38	1.76	3.43	1.41
16	3.77	1.79	3.99	1.49
32	4.17	1.88	4.53	1.57
128	4.81	1.90	5.15	1.59
512	5.43	1.97	6.08	1.71
1024	5.67	2.01	6.19	1.79
2048	5.61	1.94	6.37	1.71

Manganous Nitrate

This salt was once recrystallized, care being taken to prevent decomposition. The manganese was determined as manganese pyrophosphate.

Table LV.—Conductivity and Dissociation

	35°		50°		65°	
V	μ_v	α	μ_v	α	μ_v	α
2	139.6	52.0	171.5	49.3	205.0	47.5
8	183.8	68.5	231.7	67.0	279.9	64.8
32	216.8	80.8	277.0	80.0	338.8	78.5
128	242.0	90.2	310.5	89.7	382.8	88.7
512	256.5	95.8	335.0	96.8	413.5	95.8
1024	264.7	98.7	341.3	98.6	425.4	98.6
2048	268.3	100.0	346.3	100.0	431.5	100.0

Table LVI.—Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
2	2.13	1.53	2.23	1.30
8	3.19	1.73	3.21	1.39
32	4.01	1.85	4.12	1.49
128	4.57	1.89	4.82	1.55
512	5.20	2.02	5.23	1.56
1024	5.11	1.93	5.61	1.64
2048	5.20	1.94	5.68	1.64

Aluminium Chloride

The specimen of salt used was not recrystallized. It was, however, tested for sulphates and nitrates with negative results. The test for iron disclosed a mere trace of that element. It was only by using a fairly large amount of the substance that a positive result was obtained.

Table LVII.—Conductivity and Dissociation

	35°		50°		65°	
V	μ_v	α	μ_v	α	μ_v	α
4	231.6	45.8	296.9	42.2	361.4	37.9
8	266.8	52.8	341.6	48.6	419.1	44.0
16	291.6	58.6	381.1	54.2	470.9	49.4
64	350.3	69.3	455.5	64.8	567.3	59.5
512	429.3	85.0	567.5	80.7	730.0	76.6
1024	449.8	89.1	609.3	86.6	796.7	83.6
2048	479.9	95.0	647.5	92.1	868.5	91.1
4096	505.1	100.0	703.2	100.0	953.2	100.0

Table LVIII.—Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
4	4.35	1.88	4.30	1.45
8	4.99	1.87	5.16	1.51
16	5.66	1.91	5.99	1.58
64	7.02	2.00	7.45	1.62
512	9.22	2.15	10.83	1.91
1024	10.63	2.36	12.49	2.05
2048	11.17	2.33	14.73	2.27
4096	13.21	2.62	16.66	2.37

Aluminium Nitrate

The salt used was a fine specimen obtained from Kahlbaum. Recrystallization was effected by desiccation over sulphuric acid. The powdered salt was then allowed to stand in a vacuum over potassium hydroxide for several days. The aluminium in the mother solution was determined as aluminium oxide.

Table LIX.—Conductivity and Dissociation

	35°		50°		65°	
V	μ_v	α	μ_v	α	μ_v	α
4	219.0	45.7	276.0	42.0	338.6	37.3
8	252.0	52.6	320.8	48.8	393.9	43.4
32	306.3	64.0	394.3	60.0	487.3	53.6
128	358.0	74.7	464.4	70.7	583.9	64.3
512	407.2	85.0	535.8	82.0	685.9	75.5
1024	433.9	90.6	575.8	87.7	750.5	82.6
2048	457.4	95.5	613.3	93.4	820.9	90.4
4096	478.9	100.0	656.6	100.0	908.2	100.0

Table LX.—Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
4	3.80	1.73	4.17	1.51
8	4.57	1.81	4.87	1.52
32	5.87	1.92	6.20	1.57
128	7.10	1.98	7.97	1.72
512	8.84	2.14	10.07	1.88
1024	9.46	2.18	11.65	2.01
2048	10.40	2.27	13.84	2.25
4096	11.86	2.47	16.77	2.55

Aluminium Sulphate

The above salt was recrystallized by slowly desiccating a saturated solution over sulphuric acid. The exact strength of the mother solution was ascertained by determining the sulphur as barium sulphate.

Table LXI.—Conductivity and Dissociation

	35°		50°		65°	
V	μ_v	α	μ_v	α	μ_v	α
4	114.2	16.5	136.5	14.6	152.8	12.5
8	141.3	20.4	166.7	17.8	185.7	15.2
32	198.9	28.7	236.7	25.3	266.2	21.8
128	278.3	40.1	339.9	36.3	395.1	32.4
512	395.5	57.0	497.3	53.1	594.6	48.7
1024	478.2	68.9	613.2	65.5	740.2	60.6
2048	571.7	82.4	746.8	79.8	943.0	72.2
4096	693.5	100.0	936.1	100.0	1221.2	100.0

Table LXII.—Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
4	1.49	1.22	1.09	0.8
8	1.69	1.20	1.27	0.76
32	2.52	1.27	1.97	0.83
128	4.11	1.48	3.67	1.08
512	6.79	1.72	6.49	1.31
1024	9.00	1.88	8.47	1.38
2048	11.67	2.04	13.08	1.75
4096	16.17	2.33	19.01	2.03

Chromic Chloride (Violet Variety)

The sample of the above salt was secured from Kahlbaum, and it was purified by recrystallization from conductivity water. This was effected by the slow desiccation of a saturated solution over sulphuric acid. The powdered salt was afterwards dried over potassium hydroxide in a vacuum desiccator for a period of about a week. A gravimetric determination of the chromium as chromic oxide gave the exact strength of the original solution.

Table LXIII.—Conductivity and Dissociation

	35°		50°		65°	
V	μ_v	α	μ_v	α	μ_v	α
8	256.7	41.0	332.3	39.7	410.0	37.2
32	330.5	52.7	431.2	51.6	538.5	48.9
128	406.0	64.8	534.3	63.9	681.5	61.9
512	486.5	77.6	650.9	77.9	834.4	75.7
1024	543.7	86.7	724.2	86.6	941.3	85.5
2048	582.8	93.0	783.9	93.8	1015.7	92.2
4096	626.7	100.0	836.5	100.0	1101.4	100.0

Table LXIV.—Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
8	5.04	1.96	5.18	1.56
32	6.71	2.03	7.15	1.66
128	8.55	2.11	9.81	1.83
512	10.96	2.25	12.23	1.87
1024	12.03	2.21	14.47	1.99
2048	13.42	2.30	15.45	1.53
4096	13.99	2.23	17.66	1.60

Chromic Nitrate (Violet Variety)

This salt was recrystallized by allowing a concentrated solution to desiccate over phosphorus pentoxide. The chromium content of the mother solution was determined as chromic oxide.

Table LXV.—Conductivity and Dissociation

	35°		50°		65°	
V	μ_v	α	μ_v	α	μ_v	α
2	180.4	32.1	231.8	30.2	278.5	27.9
8	260.3	46.4	335.9	43.8	416.3	41.7
16	292.5	52.1	380.6	49.6	473.8	47.4
32	322.1	57.4	420.5	54.8	531.2	53.2
128	388.2	69.1	511.2	66.6	658.9	65.9
512	472.2	84.1	634.7	82.7	821.2	82.2
1024	514.7	91.7	692.0	90.2	894.4	89.5
2048	561.5	100.0	767.0	100.0	999.0	100.0

Table LXVI.—Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
2	3.43	1.90	3.11	1.34
8	5.04	1.93	5.36	1.59
16	5.87	2.01	6.22	1.63
32	6.76	2.09	7.38	1.75
128	8.20	2.11	9.85	1.92
512	10.83	2.29	12.43	1.96
1024	11.82	2.32	13.49	1.95
2048	13.70	2.44	15.47	2.01

Chromic Sulphate (Violet Variety)

This salt was recrystallized by slow desiccation of a concentrated solution over sulphuric acid. The powdered salt was afterwards dried in a vacuum over potassium hydroxide. The chromium in the original solution was determined as chromic oxide. The conductivity values obtained not agreeing with those of other investigators, it was deemed advisable to redetermine the chromium in the mother solution. This was done and a very good agreement with the results of the previous analysis was obtained.

Table LXVII.—Conductivity and Dissociation

	35°		50°		65°	
V	μ_V	α	μ_V	α	μ_V	α
8	110.4	19.3	128.1	14.5	139.9	12.4
32	179.0	31.3	209.7	23.8	228.5	20.2
128	265.5	46.5	328.0	37.2	370.6	32.7
512	362.2	63.4	488.8	55.5	585.3	51.7
1024	418.9	73.3	585.4	66.5	732.1	64.6
2048	458.8	80.3	713.3	80.9	905.2	80.0
4096	571.2	100.0	880.9	100.0	1132.4	100.0

Table LXVIII.—Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
8	1.18	1.07	0.79	0.62
32	2.05	1.14	1.25	0.60
128	4.17	1.57	2.84	0.86
512	8.44	2.33	6.43	1.32
1024	11.10	2.65	9.78	1.67
2048	16.97	3.69	12.79	1.78
4096	20.65	3.61	16.77	1.94

Lead Nitrate

The specimen of salt used was twice recrystallized. The purified product was dried to constant weight in the air bath at about 120°. A weighed amount of salt gave the exact concentration of the mother solution.

Table LXIX.—Conductivity and Dissociation

	35°		50°		65°	
V	μ_v	α	μ_v	α	μ_v	α
2	111.5	36.0	143.0	35.9	175.9	35.8
8	170.2	54.9	218.4	54.8	267.8	54.5
16	196.6	63.5	251.7	63.2	309.4	62.9
32	220.4	71.2	281.6	70.8	347.8	70.7
128	261.0	84.3	333.3	83.8	410.2	83.4
512	291.0	93.9	369.6	92.9	455.0	92.5
1024	300.0	96.9	385.1	96.8	477.7	97.2
2048	309.6	100.0	397.9	100.0	491.8	100.0

Table LXX.—Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
2	2.10	1.88	2.19	1.53
8	3.21	1.88	3.29	1.51
16	3.74	1.93	3.85	1.53
32	4.08	1.81	4.41	1.53
128	4.83	1.85	5.13	1.53
512	5.24	1.80	5.69	1.54
1024	5.67	1.89	6.17	1.60
2048	5.89	1.90	6.36	1.64

Nickel Nitrate

This salt was purified by three recrystallizations. The nickel content of the mother solution was ascertained by driving off the oxides of nitrogen and reducing the nickel oxide to constant weight in a stream of hydrogen.

Table LXXI.—Conductivity and Dissociation

	35°		50°		65°	
V	μ_v	α	μ_v	α	μ_v	α
2	145.5	50.9	182.7	49.4	219.7	48.4
8	188.8	66.0	239.5	64.8	291.9	64.3
32	218.4	76.4	278.3	75.3	342.7	75.7
128	243.6	85.2	310.6	84.0	386.1	85.0
512	262.0	91.7	336.2	91.0	416.0	91.6
1024	267.6	93.6	344.6	93.2	427.3	94.1
2048	285.8	100.0	369.8	100.0	453.9	100.0
4096	281.2	98.4	364.1	98.5	449.8	99.1

Table LXXII.—Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
2	2.48	1.70	2.47	1.35
8	3.38	1.78	3.49	1.42
32	3.99	1.82	4.29	1.54
128	4.47	1.83	5.03	1.65
512	4.95	1.88	5.32	1.58
1024	5.13	1.92	5.53	1.60
2048	5.60	1.96	5.61	1.52
4096	5.53	1.97	5.72	1.57

Copper Ammonium Sulphate

After one recrystallization the sulphuric acid content in the above salt was accurately determined by means of barium chloride.

Table LXXIII.—Conductivity and Dissociation

	35°		50°		65°	
V	μ_v	α	μ_v	α	μ_v	α
4	225.2	36.9	278.3	35.3	334.7	35.6
8	260.0	42.7	323.5	41.0	383.1	39.2
32	333.6	54.7	417.5	53.0	496.9	50.9
128	416.9	68.4	521.1	66.1	630.1	64.5
512	499.7	82.0	634.0	80.4	768.9	78.7
1024	546.8	89.7	697.8	88.5	850.8	87.1
2048	578.3	94.9	744.1	94.4	916.2	93.8
4096	609.5	100.0	788.3	100.0	976.8	100.0

Table LXXIV.—Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
4	3.54	1.57	3.76	1.35
8	4.23	1.63	3.97	1.23
32	5.59	1.67	5.29	1.26
128	6.96	1.66	7.27	1.39
512	8.95	1.79	8.99	1.42
1024	10.67	1.95	10.20	1.46
2048	11.05	1.94	11.47	1.54
4096	11.92	1.95	12.57	1.59

Uranyl Sulphate

As there was only a small quantity of this salt available, it was not purified. After several days' drying in a vacuum over

potassium hydroxide, the uranium in the mother solution was determined as the oxide, U_3O_8.

Table LXXV.—Conductivity and Dissociation

	35°		50°		65°	
V	μ_v	α	μ_v	α	μ_v	α
8	153.0	33.2	172.5	30.2	189.9	28.4
32	192.3	41.7	215.3	37.7	231.0	34.6
128	248.6	53.9	279.5	49.0	300.1	44.9
512	322.1	69.8	369.5	64.7	403.7	60.4
1024	360.9	78.2	421.7	73.9	471.0	70.5
2048	413.5	89.6	498.9	87.4	562.6	84.2
4096	461.4	100.0	570.7	100.0	667.9	100.0

Table LXXVI.—Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
8	1.30	0.85	1.16	0.67
32	1.53	0.79	1.05	0.49
128	2.06	0.83	1.37	0.49
512	3.16	0.98	2.28	0.62
1024	4.05	1.12	3.29	0.78
2048	5.69	1.13	4.25	0.85
4096	7.29	1.23	6.48	1.14

SPECIAL WORK

The conductivity data for chromium salts, as is also the case with other salts which are strongly hydrated and hydrolyzed, are so discordant that it was decided to do some special work on such salts. It was hoped to arrive at a possible explanation for the discordant results obtained by different investigators.

Insolubility of Jena Glass

The vessels which held the solutions used in this work were of Jena glass. As far as the solvent action of water on the glass is concerned, it is evident that by treating them in the following way all soluble matter can be removed from them up to temperatures as high as 90°. A chromic acid cleaning mixture had stood in the vessels all summer. After rinsing, they were filled with distilled water, tightly corked, and warmed to 90° for eight hours. Two of the bottles were

carefully rinsed and filled with pure water whose conductivity was known. The stoppers were tightly wired into place, and the two bottles containing the water were warmed to 90° for four hours. They were allowed to stand for two days at room temperature, and then the conductivities of the two specimens of water were determined. The results are seen best when expressed as follows: R is the resistance in the rheostat and A the reading on the bridge.

Reading for unheated water at 25°

$$R = 2000, A = 515$$

Readings at 25° for the water which had been heated in bottles to 90° for four hours

$$(1)\ R = 2000, A = 520$$
$$(2)\ R = 2000, A = 517$$

From these results and others carried out in an analogous manner, it was concluded that practically all soluble matter had been removed from our vessels.

A Dehydrolytic Time Factor in the Case of Chromic Salts

The study of the green and violet varieties of chromic salts has long been a favorite subject of investigation. The conductivity method[1] shows that the violet variety has a smaller conductivity than the corresponding concentration of the green variety, and that with increase in dilution, the conductivity of the violet salt increases at a greater rate than that of the green. To explain the greater conductivity of the green modification, several theories have been advanced. The one generally accepted to-day, and substantiated by the work of Recoura,[2] Whitney,[3] Denham,[4] Graham,[5] and others, is that the green variety contains some of the violet variety plus the products of its hydrolysis—a complex chromium salt and the corresponding acid. If this is true, the law of mass action would explain why the conductivity of the violet variety increases more rapidly with dilution than the green variety.

[1] Carnegie Institution of Washington, Publication No. **170**, p. 35.
[2] Ann. chim. phys., [7] **4**, 494 (1895).
[3] Z. physik. Chem., **20**, 40 (1896).
[4] Z. anorg. Chem., **57**, 361 (1908).
[5] Amer. Chem. Journ., **48**, 145 (1912).

For those salts which are hydrolyzed by rise in temperature, it was seen that unless the products of hydrolysis recombine as the temperature is lowered our method for the purification of salts for conductivity measurements must be changed. This point was tested out for the chromic salts.

A specimen of violet chromic chloride secured from Kahlbaum was recrystallized by allowing a solution saturated at room temperature to desiccate over phosphorus pentoxide. The chromium content of the mother solution was determined as the oxide Cr_2O_3. From the mother solution, N/32 and N/512 solutions were prepared. Four of the bottles, treated as above described to remove soluble matter, were filled with the N/32 chromic chloride solution. The stoppers of three of them were tightly wired into place. The first was warmed to 50° for two hours, the second to 65° for two hours, the third to 90° for two hours. The fourth was not heated. The heated solutions were quickly cooled to room temperature, and their conductivities determined at 35°, 50° and 65°, along with the solution which had not been heated. The following results were obtained:

V	*t*	Not heated	Heated to 50°	Heated to 65°	Heated to 90°
32	35°	330.5	331.4	342.0	415.9
32	50°	424.6	429.7	439.0	519.0
32	65°	532.4	536.9	544.6	624.2

The same process was repeated with the N/512 chromium chloride solution.

V	*t*	Not heated	Heated to 50°	Heated to 65°	Heated to 90°
512	35°	487.4	489.5	500.6	559.7
512	50°	652.2	656.7	667.7	724.6
512	65°	842.5	843.8	856.6	915.1

The results for the more dilute solutions are of the same character as those for the more concentrated. They indicate that the hydrolysis of chromium salts increases rapidly with rise in temperature. Its effect is very marked even in the N/32 solution. If we subtract the conductivities of the solutions which were not heated from the conductivities of the solutions

which were heated to 90°, we note that the effect of hydrolysis, considering the amount of salt present in the two solutions, is very much more marked in the case of the more dilute solution.

N/32 $CrCl_3$		N/512 $CrCl_3$	
35°	85.4	35°	72.3
50°	94.4	50°	72.4
65°	91.8	65°	72.6

Furthermore, it is evident that the increase in hydrolysis, at least for the N/512 solution of chromic chloride, is fairly constant, regardless of the temperature at which the conductivity readings were taken. This points to the conclusion that dehydrolysis did not take place to any appreciable extent as the solution was cooled down, and that as the temperature was again raised the conductivity of the green variety increased at about the same rate as the conductivity of the violet variety.

The following experiment was carried out to throw some light on the length of time required for the products of hydrolysis to recombine:

The N/512 solution of chromic chloride which had been heated to 90° for two hours was allowed to stand at room temperature for twenty days, and its conductivity again determined at 35°. The value found was 508, while the value found shortly after heating was 559.7. The unheated solution gave a conductivity of 487.4. A similar experiment with N/512 chromic chloride was carried out. The solution had been heated to 90° for two hours, and allowed to stand at room temperature for twenty days. Its conductivity was determined at 65°, and the value 885 was found. The conductivity shortly after heating was 915.1. That of the unheated solution was 842.5. Here we, evidently, have a dehydrolytic time factor which persists for days and, perhaps, months. From these results it is concluded that, in the purification of chromic salts, great care must be taken to keep the temperature of the solution lower than the lowest temperature at which conductivity readings are to be made. The discordant values obtained by previous investigators are perhaps due to their

method of purification and failure to take into account the dehydrolytic time factor.

Evidently, it is a matter of great importance for conductivity methods to determine whether other salts which are easily hydrolyzed show a similar phenomenon. The method by which a salt is ordinarily purified is to cool quickly a solution which is saturated at a certain high temperature. In warming solutions of such salts, it is conceivable from the previous work that, upon crystallization, they might take out of solution an excess of one of the products of hydrolysis, if the acid and base did not immediately recombine as the solution was cooled. In view of the fact that it is just such kinds of salts that have been giving trouble in conductivity measurements, it seemed desirable to carry out the following experiments:

A specimen of aluminium sulphate from Kahlbaum was recrystallized by allowing a solution saturated at room temperature to desiccate over phosphorus pentoxide. The sulphuric acid in the original solution was determined as barium sulphate. Two bottles were filled with a N/32 solution, and two more with a N/512 solution. One bottle containing the N/32 solution and another containing the N/512 solution were securely stoppered, and both warmed to 85° for two hours. These solutions were quickly cooled to room temperature and their conductivities determined as soon as possible at 35°.

Aluminium Sulphate

V	t	Not heated	Heated to 85°
32	35°	205.8	206.4
512	35°	413.6	417.0

A similar experiment was carried out with magnesium chloride. The salt was purified by recrystallization from water, and the magnesium in the mother solution weighed as magnesium pyrophosphate. Two bottles, one containing the N/32 solution, the other containing the N/512 solution, were heated to 85° for $^1/_2$ hour. Both were tightly stoppered. They were quickly cooled to room temperature, and their conductivities determined at 25°.5, along with two other solutions which had not been heated.

Magnesium Chloride

V	t	Not heated	Heated to 85°
32	25.5	187.6	188.7
512	25.5	222.7	222.5

Other salts were worked with, and results of the same general character were obtained. These results point to the conclusion that it is usually safe to heat a salt during its purification almost up to the temperature at which it will decompose without influencing the conductivity readings. The only exception to this rule which was encountered applies to the chromic salts existing in two modifications. Of course, the hydrolysis of these salts is somewhat different from that of the ordinary salts.

The Water Correction as Influenced by Various Conditions

The conductivity of the water used in making up the solutions, when multiplied by the number expressing the volume of the solution, gives the water correction which must be subtracted from the molecular conductivity of the solution to obtain the true molecular conductivity of the salt in question. It is evident that any condition influencing the conductivity of the water will have an appreciable effect when multiplied by such numbers as 2048 and 4096. It is at these dilutions that the salt is assumed to be completely dissociated, and, consequently, an erroneous water correction would vitiate the μ_∞ values for the salt, and therefore its percentage dissociation. In the following experiments, several factors influencing the water correction were taken into account.

A. The water cell was filled with conductivity water flowing at a rapid rate during a time when the air conditions in the room were much better than the normal conditions. The conductivity of the water was determined at 35° and the correction factors worked out for dilutions of N/1024, N/2048 and N/4096.

V	Correction
1024	1.74
2048	3.47
4096	6.95

B. Conductivity water was allowed to flow into a clean beaker at a rapid rate. The water was then exposed to the air for about three minutes at a time when the air conditions in the room were about normal. The time of exposure is somewhat less than the time required for making up a dilute solution and transferring it to the cell. The correction factors at 35° in this case were:

V	
1024	1.78
2048	3.56
4096	7.12

C. For this experiment, the air in the room was made less pure than normal. Three Bunsen burners were lighted for fifteen minutes, also a bottle containing ammonium hydroxide and another containing hydrochloric acid had been uncorked for an instant. The water was allowed to drop into the water cell so that a large surface of the water would be exposed to the air. The cell, holding about 60 cc., was filled during the course of two minutes. On the average a burette is hardly drained during that time. The correction factors at 35° were:

V	
1024	2.34
2048	4.68
4096	9.35

This work was repeated and results of a very similar character were obtained.

It is evident from the above work that errors larger than a per cent. may be introduced into conductivity work unless the proper water corrections are applied. The purity of the air in the room, during the times at which solutions are made up and the water cell filled, should be about the same. Furthermore, to obtain comparable results, the filling of the water cell should be so carried out that the water is exposed to the air for about the same period of time, and under the same conditions, as the more dilute solutions. These factors are more important for accurate conductivity work than has hitherto been realized. If the air conditions in the room were

good at the time the water cell was filled, and bad at the time the solutions were made up, the μ_∞ values would be too large, and too small when the reverse conditions exist. In this laboratory care is taken to have the air conditions always about the same, and the air as free from impurities as possible.

Dissociation as Measured by the Kohlrausch Conductivity Method

It is generally believed that the dissociation values, as obtained by the conductivity method, for salts which are not hydrated and hydrolyzed are correct to within the limits of experimental error. Of course, if a strongly concentrated solution of such a salt was used, the effect of viscosity would interfere with the velocities of the ions, and, consequently, the observed dissociation. It has been noted in this work that a great majority of the salts worked with did not reach complete dissociation even at a dilution of $V = 4096$. An attempt to work at dilutions beyond this proved to be impractical. Large experimental errors are involved in working with such small quantities of substance, and the effect of the air conditions on the water correction is very great.

It was noted, from the dissociation values obtained in this work, that the percentage difference between the μ_∞ value and the molecular conductivity of the next more dilute solution, as a rule, showed an increase with rise in temperature.

To throw more light upon the correctness of the above observation, some carefully prepared solutions of salts but little hydrolyzed and hydrated in dilute solutions were used. They were pure sodium chloride and pure sodium perchlorate. Special care was taken, as has already been explained, to apply the proper water correction.

For sodium chloride the following results were noted:

V	0°	12°.5	25°	35°
512	62.3	...	...	...
1024	63.2	88.6	116.9	142.6
2048	63.4	89.5	118.4	143.8
4096	63.6	90.2	120.0	145.5

The results for sodium perchlorate are very similar. They have already been tabulated (Table XVII).

It is evident that, as the temperature rises, the percentage increase in conductivity obtained by subtracting from the μ_∞ value the molecular conductivity of the next more dilute solution slowly becomes greater. We have reached with certainty the μ_∞ value only at 0°. For higher temperatures, it is necessary to work at greater dilutions to obtain the true μ_∞ value, and this, as we have seen, is impractical.

What is here brought out on a small scale becomes much more pronounced for salts which are strongly hydrated and hydrolyzed. The chromium and aluminium compounds illustrate this point very well (see Tables LXII to LXIX, inclusive).

If the salt does not reach a decided μ_∞ value at 0° for a dilution $V = 4096$, it is less probable that it will at any higher temperature, if for no other reason than because with rise in temperature the association of the solvent and its dielectric constant become less, and consequently its dissociating power is less. If the salt is strongly hydrolyzed or polymerized, the further removed from the true μ_∞ value will be the μ_v value obtained at a dilution $V = 4096$. Generally, in the dilute solutions, rise in temperature very greatly increases the effect of any one of these factors, and causes the true μ_∞ value to become more and more removed from the μ_v value obtained at a dilution $V = 4096$.

Hydrolysis is probably the chief factor in making it appear that a salt is not completely dissociated in our very dilute solutions. Aqueous solutions of many salts show an acid or basic reaction at ordinary temperatures. If we consider the case of ammonium chloride dissociated into ammonia and hydrochloric acid gas at high temperatures, we perhaps have a picture of how a strong acid and strong base in aqueous solution may exist in equilibrium with the salt molecules and water at high temperatures. As is well known, the effect of dilution and rise in temperature is to increase the hydrolysis. Consequently, at high temperatures to reach that point where there is no further increase in conductivity, it would be necessary to work with exceedingly dilute solutions. A large number of salts are but little hydrolyzed or polymerized in dilute solutions, and in such cases we can reach μ_∞ values

which are close to the correct ones. The presence of hydrated ions would necessarily make the observed dissociation too low. It does not seem probable that conductivity methods will, in the near future, be modified so that we can measure accurately the dissociation of salts strongly hydrated, hydrolyzed or polymerized. As a means of studying solutions, and obtaining the dissociation of electrolytes neither strongly hydrated, hydrolyzed nor polymerized, the conductivity method has been and probably will continue to be of great service.

DISCUSSION OF THE CONDUCTIVITY TABLES

Conductivities

Several of the salts studied in this investigation showed conductivities that are very interesting. Perhaps most interesting of all is that of ammonium acid sulphate. It is a ternary salt showing small dissociation in concentrated solutions. Its exceptionally high conductivity is probably due to the presence of the hydrogen ion. Because of small hydration, hydrolysis and depolymerization in concentrated solutions its conductivity is little increased by rise in temperature. At a dilution $V = 32$, hydrolysis and depolymerization evidently become very marked, and from then on its conductivity increases rapidly with rise in temperature and increase in dilution.

The high conductivity of potassium phosphate cannot fail to attract attention. It is a quaternary electrolyte strongly dissociated in concentrated solutions. Evidently, its complex ions break down in concentrated solutions, causing considerable hydrolysis. At the dilution $V = 512$ there is no further increase in conductivity with rise in temperature and increase in dilution. This is the only salt studied that gave clean cut μ_∞ values. It should be noted that it crystallizes without water, and, therefore, is but little hydrated in solution, and that the breaking down of its complex ions, giving rise to hydrolysis, produces its maximum effect in fairly concentrated solutions.

The conductivities of the aluminium and chromium compounds are very high and strikingly similar. The presence of a large number of ions, hydration and hydrolysis, condition

the large conductivity of these salts. The conductivity of aluminium sulphate in concentrated solutions is much less than that of either the nitrate or chloride. The same applies to the chromium salt, as does also the following. In dilute solutions, probably due to depolymerization and hydrolysis, the conductivity of the sulphates is much greater than that of the chlorides or nitrates.

Due to the greater weight of the anion and the smaller degree of dissociation, the conductivity of sodium chlorate is less than that of sodium chloride. That of sodium perchlorate is slightly greater than the conductivity of sodium chlorate, because of its greater dissociation. The conductivities of sodium chlorate and sodium perchlorate are less than the conductivities of potassium chlorate and potassium perchlorate. Since the dissociations of the sodium salts are greater than those of the potassium salts, and the potassium cation has a larger mass and atomic volume than the sodium cation, it would be a difficult matter to explain the above fact without the solvate theory. The sodium ion is more hydrated in solution than the potassium ion, and must draw with it, through the solvent, a more complex hydrate, which necessarily decreases its velocity. It should be noted that sodium perchlorate crystallizes with one molecule of water.

Potassium perchlorate is dissociated to a greater extent than potassium chlorate, except at o°. Its conductivity is at all temperatures higher than that of potassium chlorate for the corresponding dilutions.

Dissociations

With the single exception of potassium phosphate, dissociation decreases with rise in temperature, as we should expect from the Thomson-Nernst hypothesis and the relation pointed out by Dutoit and Aston. In the case of potassium phosphate, there is a marked increase in dissociation with rise in temperature except for the most concentrated solution. Contrary to the usual course of events, ionic complexes appear to be more rapidly broken down at a low temperature than at a high one. As the complex breaks down hydrolysis takes

place. It may be found that the increase is due to an abnormal exothermic heat of dissociation of this salt. It is evident from the results that the conductivity of the N/32 solution at 0° increases more rapidly with dilution than at any higher temperature.

The dissociations of salts of metals in the same group having a similar chemical composition are of the same order of magnitude. As a general rule, the sulphates in concentrated solutions are less dissociated than the corresponding nitrates and chlorides. This is probably due to the polymerization of the sulphates. Salts of metals in the second group are dissociated considerably less than salts of the alkali metals, under the same conditions of temperature and dilution. As a rule, the dissociation of any chloride, nitrate, sulphate, etc., decreases as the valence of its cation increases.

According to conductivity measurements, it is only the salts that are strongly hydrolyzed and hydrated that show any marked decrease in dissociation with rise in temperature. The sulphates of chromium and aluminium show a very marked decrease. It is probably due to the fact that with rise in temperature and dilution the polymers are rapidly broken down. If it were possible to measure the true μ_∞ value of these salts, the decrease in dissociation with rise in temperature, as measured by the conductivity method, would be much greater than that indicated by the tabulated results.

Temperature Coefficients

Temperature coefficients in conductivity units, as Jones and his coworkers have often pointed out, were found to increase with rise in temperature and increase in dilution. Ammonium acid sulphate presents a remarkable exception to this rule. Its coefficients not only decrease, but for a solution of a concentration $V = 512$ or less, and the temperature range 35°–65°, its coefficients are negative. In concentrated solutions and over the temperature range 35°–65°, chromium, aluminium and uranyl sulphates also showed decreasing temperature coefficients. Why the conductivity of the salt should begin to increase less

rapidly at these high temperatures than it does at a lower temperature is unknown.

Ammonium acid sulphate, for the concentrated solutions, shows but a very small increase in conductivity with rise in temperature. Its increase is greatest the lower the temperature range. If the conductivity of its 0.5 N solution increased with rise in temperature at the same rate as that for chromic nitrate, we would have at 65° a conductivity of over 600 instead of 235.5. The small increase in conductivity of the concentrated solutions indicates small hydrolysis and hydration. The depolymerization of the molecules must also be small. With increase in dilution some one of these factors, or, possibly, all of them act so as to increase greatly the conductivity with rise in temperature. In these dilutions temperature coefficients approaching more nearly to the normal coefficients are obtained. This points to the conclusion that the presence of a large number of unionized molecules are more capable of holding in check, with rise in temperature, the factors that ordinarily cause conductivity to increase with rise in temperature. The nature of sulphates in aqueous solution is not well understood, and merits closer and more elaborate study.

Large temperature coefficients are for the most part conditioned by hydration and hydrolysis. There two factors are evidently closely connected. It may be that water of hydration is more readily dissociated than water which is not in combination with the dissolved particles. The salts that are most strongly hydrated are, as a rule, the ones that are strongly hydrolyzed and most soluble. Jones and his coworkers[1] have already pointed out a number of relations existing between temperature coefficients of conductivity and the solvate theory of solution. The relations which they have discovered are confirmed by this work.

The remarkable increase in the temperature coefficients of conductivity of chromium and aluminium sulphates with rise in temperature and increase in dilution must attract attention. They finally reach values greater than those of any other salt

[1] Carnegie Institution of Washington, Publication No. 60, pp. 77–83.

studied. In dilute solutions, rapid depolymerization probably takes place with rise in temperature. The complex hydrates are readily broken down and hydrolysis increases. In concentrated solutions the effect of these factors with rise in temperature is very small.

Not much of interest can be deduced from the temperature coefficients in per cent. Jones[1] has pointed out that where $V = 8$ and the temperature range 25°–35°, the average value of the coefficient for a large number of widely different compounds is close to 2. Without an exception the temperature coefficients of conductivity in per cent. decrease with rise in temperature. Here, again, the coefficients of the sulphates are abnormal. Ammonium acid sulphate, chromic sulphate, uranyl sulphate and aluminium sulphate show negative coefficients in concentrated solutions. Those of chromium, aluminium and uranyl sulphates pass through a minimum. Ordinarily, a salt strongly hydrated and hydrolyzed shows a decided increase in the percentage temperature coefficients with increase in dilution. Those for salts not hydrated, hydrolyzed or polymerized are fairly constant.

SUMMARY

1. Some of the more important relations earlier pointed out by Jones and his coworkers, which the results obtained in this work confirm, are as follows:

Conductivity increases with temperature and dilution.

As a rule, temperature coefficients in conductivity units increase with rise in temperature. Salts strongly hydrated have large coefficients, those not strongly hydrated have small coefficients. The temperature coefficients are of the same order of magnitude for salts having approximately the same hydrating power. They increase with dilution, and the increase is greatest for those substances with large hydrating power.

With but one exception dissociation was found to decrease with rise in temperature.

Temperature coefficients in per cent. decrease with rise in temperature.

[1] Carnegie Institution of Washington, Publication No. **170**, pp. 77–83.

2. Abnormal and striking relations appearing in many of the conductivity tables have been pointed out, and in many cases satisfactory explanations, based upon what we to-day know in regard to the nature of solution, could be offered.

3. A dehydrolytic time factor in the case of chromic salts was observed. It was pointed out that in purifying a chromic salt for conductivity work, it must not be heated to a temperature higher than that at which its conductivity is to be taken, since the dehydrolysis time factor persists for months.

4. Other salts readily hydrolyzed were tested for dehydrolytic time factors. It was concluded that in purifying such salts it is safe to heat their solutions up to temperatures not far from the temperature at which they would decompose.

5. The effect of the air conditions on the water correction was brought out in a quantitative way, and other suggestions made to improve the accuracy of conductivity measurements.

6. The influence of hydration, hydrolysis and polymerization on conductivity measurements has been discussed, and it is concluded that the Kohlrausch conductivity method is not a good one for measuring the dissociation of sulphates which are strongly polymerized, nor for measuring the dissociation of any electrolyte which is at the same time hydrated and hydrolyzed.

BIOGRAPHY

The author of this dissertation was born in Ballston Spa, New York, May 23, 1887. After graduating from the High School of his native town, he entered Brown University in the Fall of 1906. In June of 1910 he received the degree of Bachelor of Philosophy. The following Fall he entered Johns Hopkins University as a graduate student in chemistry, taking as his subordinate subjects Physical Chemistry and Geology. During the second year of his training at the Johns Hopkins University, he was lecture assistant to Dr. Gilpin. For the year 1912–1913 he was appointed a Fellow in Chemistry.